

(19)  Canadian  
Intellectual Property  
Office

An Agency of  
Industry Canada

Office de la Propriété  
Intellectuelle  
du Canada

Un organisme  
d'Industrie Canada

(11) **CA 2 352 776**

(13) **A1**

(40) 08.06.2000

(43) 08.06.2000

(12)

(21) 2 352 776

(22) 29.11.1999

(51) Int. Cl. 7: **C01B 3/58, B01J 8/04,  
B01J 19/24**

(85) 31.05.2001

(86) PCT/GB99/03958

(87) WO00/32513

(30) 9826222.3 GB 01.12.1998

(71) JOHNSON MATTHEY PUBLIC LIMITED  
COMPANY,  
2-4 Cockspur Street  
Trafalgar Square  
SW1Y 5BQ, LONDON, XX (GB).

(72) PIGNON, JOHN FREDERICK (GB).  
GRAY, PETER GEOFFREY (GB).

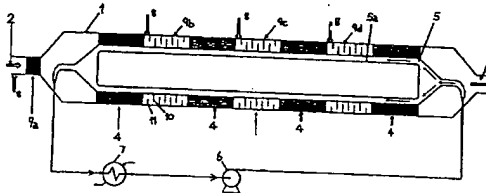
(74) RIDOUT & MAYBEE

(54) CUVE DE REACTION ET PROCEDE PERMETTANT D'ELIMINER LE MONOXYDE DE CARBONE DANS  
L'HYDROGENE

(54) REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN

(57)

<sup>222</sup>A reactor vessel (1) contains one or more selective oxidation stages and has <sup>2</sup>counter-current cooling (5, 6, 7), each stage having an inlet for feedstock <sup>2</sup>such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as <sup>2</sup>oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone <sup>2</sup>(4), preferably containing a metal support carrying a selective oxidation <sup>2</sup>catalyst. A compact reformer with a very low pressure drop is suitable for <sup>2</sup>producing hydrogen for fuel cell.<sup>2</sup>



**BEST AVAILABLE COPY**



Office de la Propriété  
Intellectuelle  
du Canada  
Un organisme  
d'Industrie Canada

Canadian  
Intellectual Property  
Office  
An agency of  
Industry Canada

CA 2352776 A1 2000/06/08

(21) 2 352 776

(12) DEMANDE DE BREVET CANADIEN  
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 1999/11/29

(87) Date publication PCT/PCT Publication Date: 2000/06/08

(85) Entrée phase nationale/National Entry: 2001/05/31

(86) N° demande PCT/PCT Application No.: GB 99/03958

(87) N° publication PCT/PCT Publication No.: WO 00/32513

(30) Priorité/Priority: 1998/12/01 (9826222.3) GB

(51) Cl.Int.<sup>7</sup>/Int.Cl.<sup>7</sup> C01B 3/58, B01J 19/24, B01J 8/04

(71) Demandeur/Applicant:

JOHNSON MATTHEY PUBLIC LIMITED COMPANY, GB

(72) Inventeurs/Inventors:

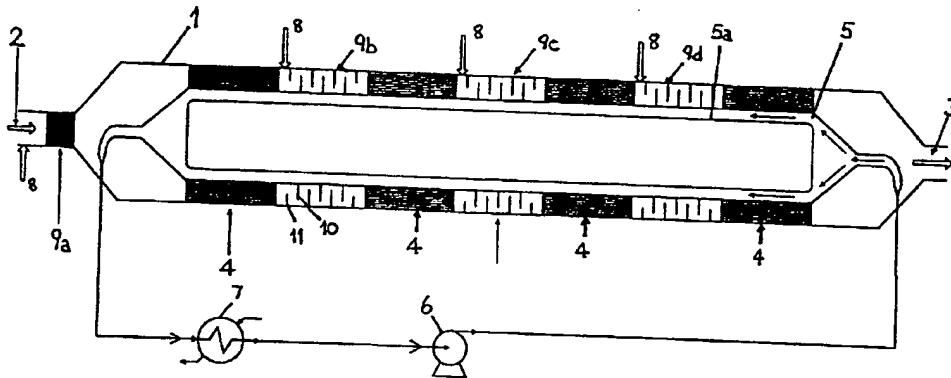
PIGNON, JOHN FREDERICK, GB;

GRAY, PETER GEOFFREY, GB

(74) Agent: RIDOUT & MAYBEE

(54) Titre : CUVE DE REACTION ET PROCEDE PERMETTANT D'ELIMINER LE MONOXYDE DE CARBONE DANS  
L'HYDROGENE

(54) Title: REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN



(57) Abrégé/Abstract:

A reactor vessel (1) contains one or more selective oxidation stages and has counter-current cooling (5, 6, 7), each stage having an inlet for feedstock such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone (4), preferably containing a metal support carrying a selective oxidation catalyst. A compact reformer with a very low pressure drop is suitable for producing hydrogen for fuel cell.

Canada

<http://opic.gc.ca> • Ottawa-Hull K1A 0C9 • <http://cipo.gc.ca>

OPIC • CIPQ 191

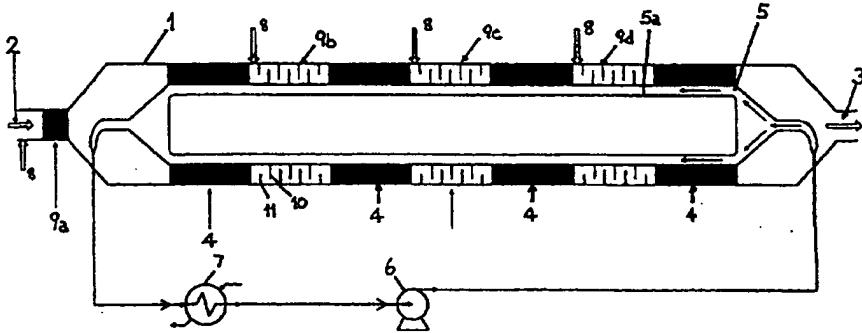
OPIC



CIPQ

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup>:</b> <b>C01B 3/58, B01J 19/24, 8/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/32513</b> <b>(43) International Publication Date:</b> 8 June 2000 (08.06.00)
<b>(21) International Application Number:</b> PCT/GB99/03958 <b>(22) International Filing Date:</b> 29 November 1999 (29.11.99)  <b>(30) Priority Data:</b> 9826222.3 1 December 1998 (01.12.98) GB  <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GRAY, Peter, Geoffrey [AU/GB]; The Linney, Blounts Court Road, Sonning Common, Reading RG4 9RS (GB). PIGNON, John, Frederick [GB/GB]; 14 Castle Close, Benson, Oxon OX10 6SN (GB).  <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).	<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN   <b>(57) Abstract</b> <p>A reactor vessel (1) contains one or more selective oxidation stages and has counter-current cooling (5, 6, 7), each stage having an inlet for feedstock such as CO-contaminated hydrogen (2), an inlet for a second feedstock such as oxygen or air (8), gas mixing means (9a, 9b) and a catalytic reaction zone (4), preferably containing a metal support carrying a selective oxidation catalyst. A compact reformer with a very low pressure drop is suitable for producing hydrogen for fuel cell.</p>		

WO 00/32513

PCT/GB99/03958

1

## REACTOR AND PROCESS FOR REMOVAL OF CARBON MONOXIDE FROM HYDROGEN

5

The present invention concerns an improved reactor, more particularly it concerns a reactor particularly adapted for and suitable for certain selective oxidation reactions.

We have previously developed certain selective oxidation processes for the removal of residual carbon monoxide in hydrogen-containing gases intended as feedstock for fuel cells. Such processes are disclosed and claimed in for example, PCT/GB98/02873. It has become well established that hydrogen-fuelled fuel cells require very low proportions of carbon monoxide, which acts as a catalyst poison and degrades performance of the fuel cell. Desirably, the amount of CO is less than 10 ppm. If a liquid fuel is reformed to form a hydrogen-containing fuel, levels of CO are produced which may vary about 0.5-5mol%, so that it becomes necessary to attenuate such CO levels. As mentioned in the above International Application, catalytic selective oxidation reactions are highly exothermic with the result that increasing reaction temperatures lead to increasing loss of valuable hydrogen due to competing reactions.

20

There remains a need for a catalytic selective oxidation reactor which permits good temperature control yet is simple, effective and inexpensive to manufacture. Although hydrogen "cleaned-up" by the reactor of the present invention may be used as fuel cell fuel, there are many other uses for such hydrogen. Also, although the reactor is particularly suitable for the cleaning up of reformat (which may be from methanol, other oxygenated fuels, gasoline or other hydrocarbon fuels), it is not limited to such use. Accordingly, the present invention provides a reactor for catalytic selective oxidation, comprising a reactor vessel with counter current cooling and at least one stage, each stage provided with an inlet for a first feedstock, e.g. CO contaminated hydrogen, an inlet for a second feedstock, e.g. oxygen-containing gas, gas mixing means and a catalytic reaction zone, preferably comprising a selective oxidation catalyst deposited on a substrate having good heat conduction properties.

25

30

The invention also provides a process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said

35

WO 00/32513

PCT/GB99/03958

2

feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation catalyst in a selective oxidation zone and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective oxidation zone, preferably to maintain the selective oxidation zone at a temperature in the range 100 to 250°C, by counter-current coolant flow.

5

The reactor, in its most preferred embodiment, has four stages and this is effective to reduce a reformat having a CO content of 1 to 2% to below 10ppm. In other embodiments, there may be 2 to 10 stages.

10

The reactor is suitably in the form of a vessel in which the reaction zones are generally annular in shape, and provided with internal and/or external liquid cooling. Cooling is preferably provided by internal cooling using water, which is suitably under pressure to prevent boiling at the temperatures generated. Other liquid coolants, or forced air cooling may be used if desired. According to specific reactor designs, heat removal may be enhanced by increasing heat exchange surface areas by corrugation or other established means. Heat removal may be altered by altering the flow of coolant and/or altering the quantity of heat removed from the coolant by means of a heat exchanger.

15

Each reaction zone suitably comprises a metallic catalyst support ("monolith") of generally honeycomb construction, as is in common use in automobile exhaust gas catalysis. These may have 50 to 1200 cells per square in cell density, preferably 200 to 600 cpsi, and may be of a variety of types of stainless steel. In general, the present invention does not result in the reaction stages reaching the higher temperatures generally met with in exhaust gas catalysis (e.g. 500-900°C), but the material should be capable of resisting temperature excursions. An alternative reaction zone design utilises what has become known as "static mixers" which combine a very high degree of gas agitation and mixing, resulting in non-laminar flow, with relatively low pressure drop. Such static mixers may be manufactured from a variety of metals and are commercially available. However, it is presently preferred to use a honeycomb monolith.

20

25

30

The reaction zone desirably carries a selective oxidation catalyst comprising a platinum group metal, especially comprising platinum and/or rhodium, carried on a high

WO 00/32513

PCT/GB99/03958

3

surface area metal oxide support, such as alumina. The metallic catalyst support may be coated by generally known methods with a slurry of oxide support, dried and fired, and then impregnated with the catalytically active components, before a final firing. Such procedures are in themselves known, and do not form part of this invention.

5

The invention will now be described with reference to the accompanying drawing which shows a cross-section of one embodiment of the present invention.

An essentially cylindrical metal vessel, made by pressing two halves and seam-welding, has a main gas inlet, 2, for reformat gas, and an outlet, 3, for cleaned gas. The vessel has a number of annular reaction zones, 4, each consisting of an annular wound corrugated catalyst support. The vessel further has an internal water jacket, 5, between a spacer and the shell and this is supplied with cooling water by means of a water circuit comprising a circulating pump, 6, and a heat exchanger, 7. The heat exchanger is desirably used to recover heat in an integrated system e.g. in an integrated combined heat and power system. The vessel further is provided with four air inlets, 8, each providing pre-determined (for a steady-state operation) levels of air (that is reaction oxygen; air is generally suitable). Although not preferred, controlled amounts of oxygen, according to one or more feedback or feed forward controls detecting gas flow levels and CO levels may be used. Downstream of each air inlet is a gas mixing zone, 9a, 9b, 9c and 9d. Zone 9a is suitably a static mixer, but zones 9b, 9c and 9d are preferably alternating annular mixing vanes, 10, and discs, 11, having gas flow holes, as illustrated in Figs 2 and 3. It should be noted that for simplicity only four vanes and four holes are shown, but more, e.g. six or eight, may be used. Such vanes and discs may be manufactured by pressing to form a sleeve which may be fitted and brazed or welded onto the jacket 5 with the intention that each gas mixing zone also serves to remove heat from the reaction gases leaving each reaction zone. Although the schematic drawing of the reactor shows each reaction zone and gas mixing zone of the same size, these may be designed to differ according to the amount of heat to be removed. Additionally, each reaction zone may incorporate different and/or different loadings, of catalyst. Each metal catalyst support monolith suitably has 300-400 cells per sq.in. and is coated with a washcoat comprising ~36wt% alumina solids of D50 of approx 5µm and D90 of approx 16µm, to deposit approx 3g/m<sup>3</sup>. After drying and firing, the coated monolith was impregnated with

WO 00/32513

PCT/GB99/03958

4

a platinum salt solution to result in 5% by wt of Pt deposited on the alumina. The resulting coated monolith was again dried and fired before being assembled into the reactor.

Initial studies indicate that a reformat containing 1-2% CO in admixture with H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, water vapour with a small proportion of unreacted reformer feedstock (e.g. CH<sub>3</sub>OH, CH<sub>4</sub>, gasoline), at 180°C may be converted to a feed gas suitable for a fuel cell, containing below 10ppm CO, and at 140°C.

The reactor of the invention is compact and exhibits relatively low pressure drop. Manufacturing costs are relatively low. The reactor is believed to be suitable for mobile or automobile uses as well as stationery uses. It is presently envisaged that the reactor shell will be lagged to control heat loss and prevent injury. The reactor can be manufactured simply and inexpensively, using pressed and welded parts. It is desirably operated to achieve low pressure drop, and the particular embodiment illustrated is designed for a gas hourly space velocity of approx. 30,000h<sup>-1</sup> gas throughput.

The reactor as described may be altered in a variety of ways without departing from the central inventive concept.

The invention is now illustrated below in a working example of a two-stage reactor, fed with a synthetic reformat gas mixture containing N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. Each of the two stages consists of a mixing zone with three off-set spiral vanes, followed by air injection accomplished through a number of apertures in an annular ring, producing a swirling, mixing gas. The thus mixed hydrogen and air mixture passes through an annular metal honeycomb support mounted on a central cooling jacket. The cooling jacket is fed counter-current to the flow of hydrogen with a heat transfer fluid, conveniently water under pressure, and the metal honeycomb support is mounted in good heat exchange contact with the cooling jacket. The metal honeycomb carries a selective oxidation catalyst. Gas may be extracted for analysis between the two stages and/or after the second stage. By setting the composition of the feedstock gas mixture according to that analysed after the first or second stage, the test two-stage reactor can model a three or four stage reactor.

WO 00/32513

PCT/GB99/03958

5

The detailed operating conditions and other experimental detail for one typical run of the above reactor now follow. It was remarkable that the pressure drop across the whole of the est reactor was about the measurement limit of the gauges being used, and was of the order of 1.5-3mbar (150-300Pa), at the two throughputs tested. This indicates that the reactor is very efficient, compact and requires very little energy to operate.

1. Each catalyst support was an annular of internal diameter 3.85in (9.78cm), external diameter 5.85in (14.86cm) and 3.0in(7.62cm) length, made from "Fecralloy" steel and having 500 cells per sq in. Each support had been washcoated with alumina washcoat as used in exhaust gas catalytic convertors, followed by loading with 5% by wt of the alumina of Pt. Conventional manufacturing techniques were used.
2. The synthetic reformat had the compositions: 48%N<sub>2</sub>(dry), 40%H<sub>2</sub> (dry), 10%CO<sub>2</sub>(dry), 0.5-1.5%CO (dry) and 13% H<sub>2</sub>O (of total flow). Two levels of CO concentration were chosen, a higher level to represent the output from autothermal reforming, and a lower level to represent the output from steam reformer or an optimised reformer, and two levels of throughput stated to be Nominal 3kWe (1kilowatt equivalent = 1,000 l/hr of H<sub>2</sub>) and Nominal 6kWe, equal to 7,5000 l/hr of dry reformat and 15,000 l/hr of dry reformat respectively (8,620 l/hr and 17,240 l/hr of wet reformat).

It is plain from these results with a two-stage reformer that the compact and efficient reformer of the invention will be effective to remove CO from Hydrogen to any desired level, by conventional optimisation and especially by matching the number of stages to the requirements of the fuel cell system or other usage of the purified hydrogen.



WO 00/32513

6

PCT/GB99/03958

## TWO-STAGE ANNULAR SELOX REACTOR TEST RESULTS

SECOND STAGE											
FIRST STAGE											
Ex No.	Power kW <sub>e</sub>	CO in %, dry	Air in, slm	Temp in C	Temp out, C	CO out %, dry	Air in, slm	Temp in, C	Temp out, C	CO out ppm dry	Sel**
1	3	1.5	4	125	212	0.60	2	167	212	1610	0.696
2	3	1.5	4	127	214	0.60	3	167	217	740	0.640
3	3	1.5	4	125	210	0.60	4	169	227	950	0.556
4	3	1.5	3	125	149	0.81	3	129	175	1840	0.684
5	3	1.5	5	128	215	0.34	3	161	220	290	0.582
6	3	0.5	2	143	176	0.122	0.5	138	145	232	0.579
7	3	0.5	2	141	167	0.122	0.8	127	136	29	0.540
8	3	0.5	2	140	161	0.122	1.0	121	130	28	0.505
9	3	0.5	2	141	172	0.122	1.2	131	146	55	0.472
10	3	0.5	1.5	142	166	?	1.0	134	157	373	0.562
11	3	0.5	2.5	142	179	?	1.0	138	150	50	0.433
12	6	0.5	4	138	167	0.130	1	148	176	722	0.520
13	6	0.5	4	138	162	0.130	2	140	185	51	0.503
14	6	0.5	4	138	166	0.130	3	146	198	105	0.428
15	6	0.5	6	138	205	62ppm	0	176	174	62	0.502

\*\* Sel: (Selectivity) = CO consumed/2 x O<sub>2</sub> consumed

**CLAIMS**

1. A catalytic selective oxidation reactor, comprising a cylindrical reactor vessel (1) with counter current cooling means (5,6,7) and at least one stage, each stage being  
5 provided with an inlet for a first feedstock (2), and inlet for a second feedstock (8), gas mixing means (9) and a catalytic reaction zone (4), wherein the reaction zone comprises a selective oxidation catalyst deposited upon a metal support.
2. A reactor according to claim 1, wherein the metal support is mounted in good heat  
10 exchange contact with the cooling means.
3. A reactor according to any one of the preceding claims, wherein the metal support is a metal monolith.
- 15 4. A reactor according to any one of the preceding claims, wherein the cooling means comprises a central jacket mounted within the reactor.
5. A reactor according to claim 4, wherein the central jacket is connected via a coolant circuit to an external heat exchanger.
- 20 6. A reactor according to claim 4 or 5, wherein the central jacket is connected via a coolant circuit to a circulating pump.
7. A reactor according to any one of the preceding claims, wherein the catalytic reaction  
25 zone(s) is/are annular and surround a central cooling means.
8. A reactor according to any one of the preceding claims, having from 2 to 10 stages.
9. A reactor according to claim 8, having four stages.
- 30 10. A reactor according to any one of the preceding claims, wherein the gas mixing means comprise annular mixing vanes or discs.

AMENDED SHEET

11. A reactor according to any one of the preceding claims, connected to the output from a reformer such that CO is removed from the output gas to a level where the output from the reactor may be fed to a fuel cell.
- 5 12. A process for the removal of quantities of CO from a hydrogen feedstock by partial oxidation, comprising at least one step of admixing said feedstock with a quantity of oxygen, passing the resulting mixture over a selective oxidation zone comprising a selective oxidation catalyst on an annular metal support, and recovering a hydrogen product with reduced content of CO, whilst simultaneously cooling the selective  
10 oxidation zone by counter-current coolant flow.
13. A process according to claim 12, wherein the selective oxidation zone is maintained at a temperature in the range 100 to 250°C.
- 15 14. A process according to claim 12 or 13, providing hydrogen to a fuel cell.

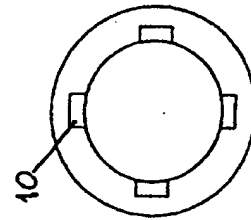
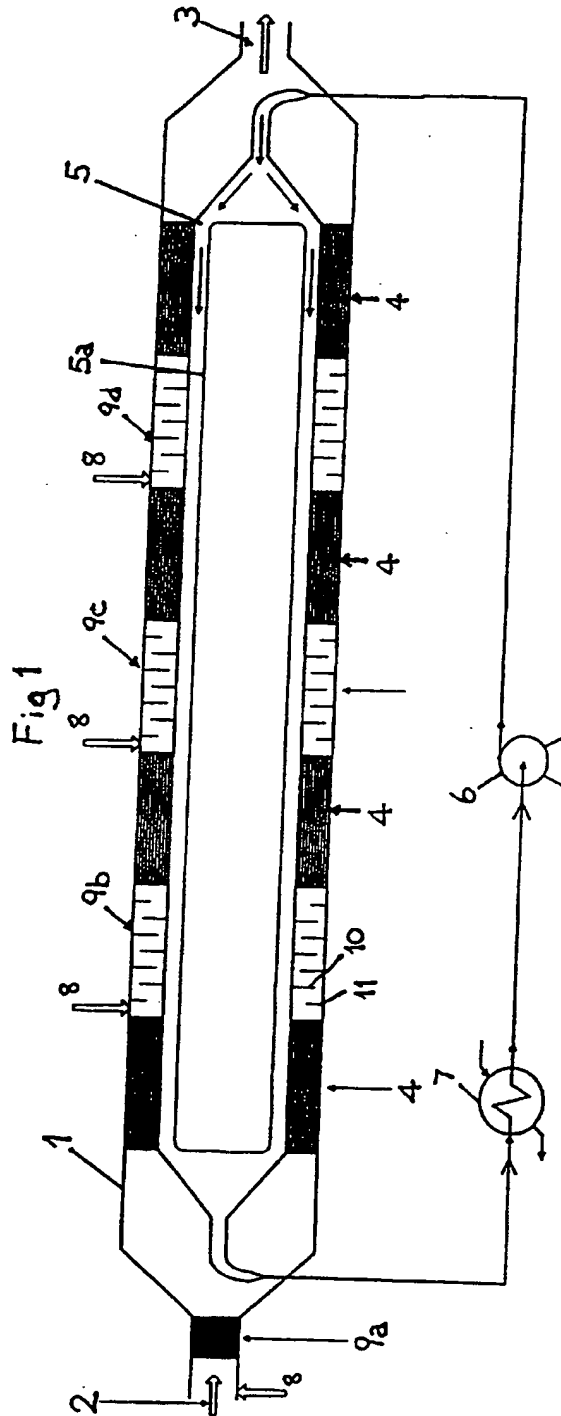


Fig 3

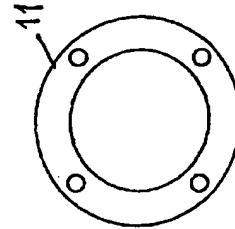


Fig 2